Surface States on Tungsten

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(Received 27 August 1970)

The energy distribution of field-emitted electrons from single-crystal faces of tungsten exhibits structure which is extremely sensitive to surface contaminants. The structure for the (100) plane has the correct shape and energy expected for surface states resulting from spin-orbit–split bands. These results are in good agreement with recent theoretical predictions.

There have been several recent theoretical papers predicting that surface states can exist in d-band metals near the crossover of s and d bands of the same symmetry.[1-4] This paper reports the first direct experimental evidence of surface states on clean single-crystal faces of tungsten. Total energy distributions of field emitted electrons from single-crystal planes reveal surface-dependent electronic structure in good agreement with the surface state model of Forstmann, Pendry, and Heine.[3,4] The agreement is especially striking on the (100) plane where the relativistic energy-band calculations of Loucks[5] can be applied.

The total energy distribution of field-emitted electrons from a single-crystal plane of a free-electron metal is[6]

$$j_0'(\epsilon) = Ae^{+\epsilon/d}/(1 + e^{+\epsilon/kT}), \qquad (1)$$

$$\epsilon = E - E_F,$$

$$1/d \propto \varphi^{1/2}/F,$$

where φ is the work function, F is the applied field, and E is the energy in electron volts measured from the bottom of the band, with E_F denoting the Fermi energy. Typically, values for $1/d$ are approximately 7 eV^{-1}. It is apparent from Eq. (1) that the energy distribution is predominantly exponential. In order to illustrate deviations of the measured energy distribution $j'(\epsilon)$ from the theoretical free-electron distribution, it is convenient to define an enhancement factor $R(\epsilon)$,

$$R(\epsilon) = j'(\epsilon)/j_0'(\epsilon), \qquad (2)$$

which will reveal not only deviations from free-electron behavior in the bulk, but also specific surface effects.[7]

In Fig. 1 we plot an energy distribution from the (100) plane of tungsten. The hump at $\epsilon = -0.37$ eV has been observed before,[7,8] but new structure at lower energies is revealed with an improved electron energy analyzer.[9] The Lorentzian-type

wings on the energy distribution with respect to the ideal energy distribution $j_0'(\epsilon)$ (dashed line in Fig. 1) increase with current density. This was reported by Lee and Gomer[10] for $\epsilon > 0$ but also occurs at the low-energy tail. This behavior is inherent in the field-emission process and not a property of the analyzer. The wings are probably a result of electron-electron interaction, but it yet remains to be determined whether this interaction occurs in the tunneling process, as suggested by Lee and Gomer,[10] or in the electron beam outside the metal.[11] The importance of the wings in this study is that the one below the Fermi surface places an immediate limit on the working energy range below E_F.

In Fig. 2(b) we show $R(\epsilon)$ for the (100) plane, while Fig. 2(a) is the relativistic band-structure calculation for the (100) direction of tungsten by Loucks.[5] There are three Δ_7 symmetry bands in this direction resulting in two gaps where the top band would have crossed over the lower two. The two larger peaks in the $R(\epsilon)$ plot ($\epsilon = -0.37$ eV and -1.5 eV) fall at the bottom of both of
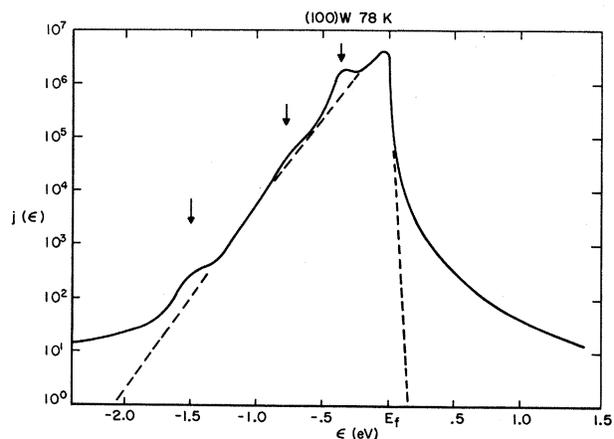
FIG. 1. Total energy distribution of field emitted electrons from (100) plane of tungsten. The dashed lines indicate a free-electron energy distribution given by Eq. (1). The ordinate represents the counts per 0.020 eV.
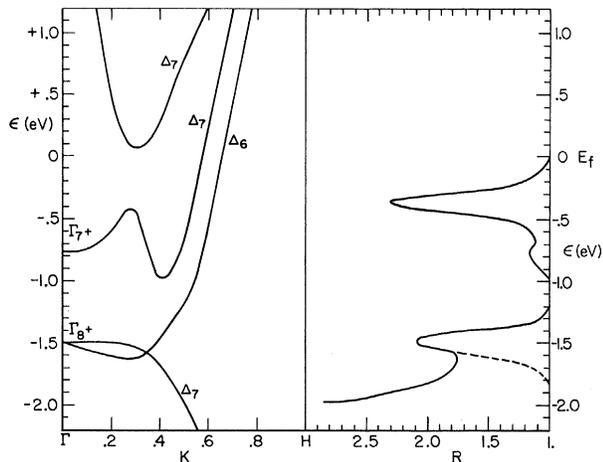
FIG. 2. (a) Relativistic energy bands for the (100) direction of tungsten calculated by Loucks (Ref. 5), showing the two gaps created by the splitting of the three Δ_7 bands. (b) The experimental enhancement factor $R(\epsilon)$ for the (100) plane of tungsten [defined in Eq. (2)].

these gaps, in qualitative agreement with the predictions of Forstmann, Pendry, and Heine.[3,4] The wing of the energy distribution causes $R(\epsilon)$ to increase dramatically for $\epsilon \lesssim -1.17$ eV making the state at $\epsilon = -1.5$ eV difficult to observe. At lower current density (low field) there is not enough current at $\epsilon = -1.5$ eV and at higher current density the wing masks this structure.

The two larger peaks in Fig. 2(b) are extremely sensitive to surface contamination. In Fig. 3 the maximum amplitude of the enhancement factor $R_{max}(-0.37$ eV) for the surface state at $\epsilon = -0.37$ eV is plotted as a function of the exposure to CO at 78 K. The sticking coefficient in this coverage range and temperature is probably constant and nearly unity.[12] Therefore the density of surface states decreases linearly with the number of adsorbates. The peak completely disappears between one-half and one monolayer. The same qualitative behavior occurs with adsorption of H_2, N_2, and O_2. Lee and Gomer[13] have also reported that Kr adsorption will remove this state. In contrast, the structure at $\epsilon = -0.78$ eV is almost insensitive to adsorption in the range of Fig. 3. This structure will disappear at larger exposures or higher temperatures, probably as a result of surface rearrangement. Most likely this structure at $\epsilon = -0.78$ eV is a ramification of the bulk d band originating at Γ_7^+.[14] But we should always remember that the band-structure calculations are for an infinite bulk crystal and the local electronic struc-
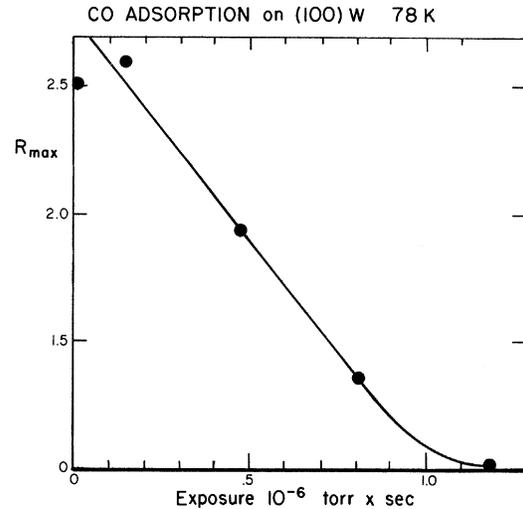
FIG. 3. The amplitude R_{max} of the $\epsilon = -0.37$ eV peak on the (100) plane [see Fig. 2(b)] as a function of exposure to CO at 77 K.

ture at the surface may be different, independent of the presence of surface states.

We have concentrated on the (100) plane of tungsten because it is probably the most interesting experimentally and major efforts have been expended theoretically[5,15] to calculate the splitting of the bands in this direction. For completeness we list in Table I the energies and widths of all the structures observed on the (110), (100), (112), (111), and (013) planes of tungsten. The maximum enhancement factors at the appropriate energies are also given. Qualitatively all the structure is consistent with what one would expect from Mattheiss's[15] band-structure calculations if band splitting was introduced. The peaks at ~−0.37 eV on the (013) and (112) planes probably originate from the same split band as the state on the (100) plane. Likewise, the peaks at ~1.5 eV on all the planes[16] are in the region

Table I. Structure in energy distribution.

Plane	ϵ	Γ	R
110	~−0.5*[a]	···	···
100	−0.37	0.16	2.4
	−0.78*[a]	···	1.17
	−1.5	~0.2	2.1
(112)	−0.69	0.18	1.5
	−1.50	~0.2	2.6
(111)	−0.70*[a]	0.4	1.5
	−1.33	0.3	1.15
(013)	−0.39	0.4	1.7
	−1.45	0.3	1.35

[a]Not as sensitive to surface contamination.

between $\Gamma_7{}^+$ and $\Gamma_8{}^+$ in Fig. 2(a).

In a previous theoretical analysis of the effects of band structure on the energy distribution of field-emitted electrons,[14] it was shown that the tunneling probability from a localized d band would be $\sim 10^{-2}$ that of the tunneling from a s band. Physically this resulted from the additional confinement of the d-wave function by the centrifugal potential barrier. The d-wave functions are contracted about the ion core and do not extend into the vacuum as far as the free-electron (s-band) wave function. We expect that the tunneling from localized d-associated surface states would be similar to narrow d bands, but if surface states are occupied, then in order to preserve charge neutrality in the unit cells of the last layer or two of the metal a charge redistribution must occur.[3] Consequently the density of s-band electrons at the surface would be decreased, increasing the ratio of the tunneling probability from the surface state relative to the free electrons. The large enhancement factor for the surface states [Fig. 2(b)] relative to the contribution from the d band ($\epsilon = -0.78$ eV) supports this argument.

Tentatively we would expect the presence of surface states and their removal upon adsorption to affect the work function in a manner not previously included in any analysis.

[1]J. B. Pendry and F. Forstmann, J. Phys. C: Proc. Phys. Soc., London 3, 59 (1970).

[2]F. Forstmann, Z. Phys. 235, 69 (1970).

[3]F. Forstmann and J. B. Pendry, Z. Phys. 235, 75 (1970).

[4]F. Forstmann and V. Heine, Phys. Rev. Lett. 24, 1419 (1970).

[5]T. L. Loucks, Phys. Rev. Lett. 14, 212 (1965).

[6]R. D. Young, Phys. Rev. 113, 110 (1959).

[7]E. W. Plummer and R. D. Young, Phys. Rev. B 1, 2088 (1970).

[8]L. W. Swanson and L. C. Crouser, Phys. Rev. Lett. 16, 389 (1966), and Phys. Rev. 163, 622 (1967).

[9]A Kuyatt-Simpson [Rev. Sci. Instrum. 38, 103 (1967)] spherical deflection analyzer has been adapted to field-emission studies. This analyzer produces higher signal-to-noise ratios below the Fermi surface than the commonly used retarding analyzer. Details will be given elsewhere.

[10]C. Lee and R. Gomer, to be published.

[11]J. Arol Simpson and C. E. Kuyatt, J. Appl. Phys. 37, 3805 (1966).

[12]C. Kohrt and R. Gomer, J. Chem. Phys. 48, 3337 (1968).

[13]C. Lee and R. Gomer, private communication.

[14]J. W. Gadzuk, Phys. Rev. 182, 416 (1969).

[15]L. F. Mattheiss, Phys. Rev. 139, 236 (1965).

[16]Because of the low current from the (110) plane we have not yet looked this far below E_F.

Anomalous Exciton Spectra in Uniaxially Deformed CuCl: Experimental Evidence for the Effect of the Stress-Induced k-Linear Term

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(Received 22 September 1970)

Anomalous exciton spectra have been observed in uniaxially deformed CuCl. The observed features, which cannot be accounted for by the previous theory, were successfully interpreted by the effect of the stress-induced k-linear terms in the energy band of CuCl, as very recently proposed by Sakoda and Onodera. Experimental evidences for this interpretation are presented.

Among several experimental means for investigating exciton states in semiconductors, the effect of uniaxial stress has been recently attracting considerable interest, mainly in view of obtaining information on the stress and spin-exchange coupling effect.[1] For the parabolic exciton at the Γ point, a general theory has been recently presented by Langer et al.[2] taking stress-exchange effect into account for cubic zinc blende and hexagonal wurtzite semiconduc-

tors. In this Letter, however, we report a new phenomenon we have observed in zinc blende CuCl, which cannot be explained by the previous theory. Essential points of the experimental results are presented here along with their interpretation in terms of the stress-induced k-linear term, very recently theoretically investigated by Sakoda and Onodera.

The uniaxial stress measurements have been made on reflection spectra of CuCl single crys-